

Adsorption of bisphenol-A, 17 β -estradiol and 17 α -ethinylestradiol to sewage sludge

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Abstract

Adsorption of bisphenol-A (CAS 85-05-7), 17 β -estradiol (CAS 50-28-2) and 17 α -ethinylestradiol (CAS 57-63-6) to activated and to inactivated sludge from wastewater treatment plants (WWTPs) was investigated, thus allowing to distinguish between pure adsorption and biosorption. For the investigated substances the determination of the adsorption kinetics is based on experiments performed according to the OECD guideline 106 and on free concentration measurements in the liquid phase. The description of the adsorption behaviour occurred via Freundlich Adsorption Isotherms. Additionally specific adsorption coefficients K_D , K_{OM} and K_{OC} were calculated. The results of these calculations were compared to K_{OC} values obtained with a HPLC method according to the OECD guideline 121. All substances showed a high adsorption affinity to the adsorbent and in spite of the application of very high initial concentrations no saturation level could be reached. Within a contact time of 24 h, no difference between the adsorption to activated and inactivated sludge could be detected. The calculated K_D values were within a range of about $K_D = 1000 \text{ l kg}^{-1}$ for the investigated compounds and showed a clear concentration dependency in the case of bisphenol-A. Adsorption was also found to depend on pH. The experimentally determined K_{OC} values of the investigated substances were significantly higher than the results obtained with the HPLC method described in OECD guideline 121.

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1. Introduction

Substances interfering with the hormone system of animals and human beings represent an issue of increasing interest in the public. According to a description by the European Commission (CEC, 1999), *an endocrine disrupter is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations.*

Two different classes of substances causing endocrine disruption can be identified. On the one hand there are natural substances, including natural sexual hormones (estrogens, progesterone and testosterone) and phytoestrogens. On the other hand we find xenobiotic substances including synthetic hormones as the contraceptive 17 α -ethinylestradiol as well as man-made chemicals and their by-products (e.g. pesticides, cleaning agents, flame retardants, etc.).

Negative adverse health effects on aquatic organisms, which could be attributed to endocrine disrupting substances (EDS), are documented in various studies (e.g. Sheffield et al., 1998; Sumpter, 1998). EDS are suspected to enter rivers, streams and surface waters through the effluents of wastewater treatment plants (WWTPs),

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wherefore the elimination of these substances in the sewage treatment plant (STP) is of elementary interest. The behaviour and the removal within WWTP depend on physicochemical properties of the observed substances and on WWTP configuration and operation. As major removal pathways pure adsorption to the sludge, biological degradation and transformation, chemical degradation and volatilization have to be distinguished (Langford and Lester, 2003).

The present article focuses on the adsorption of bisphenol-A (BP-A), 17 α -ethinylestradiol (EE₂) and 17 β -estradiol (E₂) to sewage sludge. Bisphenol-A is one of the most produced chemicals worldwide with known endocrine potential. 17 β -estradiol is the natural female sexual hormone and 17 α -ethinylestradiol is a commonly used contraceptive agent. Especially hormones, natural or synthetic, are known to cause adverse health effects in aquatic organisms already at very low concentrations of 0.1–0.5 ng l⁻¹ (Lange et al., 2001). Adsorption processes to sludge are of special interest because the excess sludge extraction represents an important removal pathway and sorption is often the first stage in biological degradation.

2. Materials and methods

2.1. Materials

The chemicals used for the experiments were purchased from Sigma-Aldrich: bisphenol-A (4,4'-isopropylidenediphenol), Aldrich 13302-7, CAS 80-05-7, EC 2012458, C₁₅H₁₆O₂ and molecular weight (MW) of 228.3 g mol⁻¹; 17 β -estradiol, Aldrich 25015-5, CAS 50-28-2, EC 2000238, C₁₈H₂₄O₂, MW 272.4 g mol⁻¹; 17 α -ethinylestradiol, Aldrich 28586-2, CAS 57-63-6, EC 2003422, C₂₀H₂₄O₂, MW 296.4 g mol⁻¹.

The chemicals were dissolved in ethanol and stock solutions of 1 and 5 g l⁻¹ were established. The spiking of sludge, water samples and standard solutions occurred with those stock solutions.

2.2. Analytical methods

Different analytical methods according to the applied concentrations were used.

Concentrations covering the higher microgram per litre (µg l⁻¹) and milligram per litre (mg l⁻¹) range were analysed using high performance liquid chromatography (HPLC) and UV detection. A water–acetonitrile solution (60:40) was used as mobile phase. Isocratic elution with a constant flow rate of 1 ml l⁻¹ at room temperature and a pressure of about 120 bar was applied. A RP-18 column (Merck LiChrospher 100 RP-18), with an

average grit size of the spherical silica gel of 5 µm and a length of 125 mm was used. The detection was performed with an UV detector at 225 nm. Due to different retention times of the three substances, the method allows simultaneous determination in one run.

This HPLC method was applied for all adsorption experiments performed with initial concentrations higher than 1 mg l⁻¹ and for the desorption experiments.

For the experiments covering the low microgram per litre (µg l⁻¹) and the nanogram per litre (ng l⁻¹) range, the following methods were applied.

Bisphenol-A samples were acidified with 1 N sulphuric acid and percolated by Isolute C18 solid phase extraction (SPE) columns at a flow rate of ≈ 10 ml min⁻¹, previously conditioned by 5 ml methanol and 5 ml water. Prior to extraction a surrogate standard was added. After drying with nitrogen, the compounds were eluted by 5 ml acetone and 5 ml methanol/methyl-*tert*-butylether (1:9). The extracts were evaporated below 0.5 ml by nitrogen and filled up to a final volume of 1 ml with acetonitrile. 10 µl of internal standard were added prior to analysis. Aliquots of 10 µl were used for analysis with LC-MS/MS applying electrospray ionisation. The limit of detection (LOD) was 10 ng l⁻¹.

The sample preparation for the determination of the hormones included liquid–liquid extraction with ether followed by SPE with ENV+ cartridges eluted by methanol. After evaporation to dryness a derivatization with dansylchloride occurred. Prior to extraction surrogate standards were added. The analysis was performed using LC-MS/MS by an injection volume of 20 µl. Ionisation of the analytes was done by electrospray ionisation in positive mode. The LOD for the estrogens was 1 ng l⁻¹.

Detailed descriptions of the methods applied for analysis in the lower concentration ranges are reported in ARCEM (2002) and in Scharf et al. (2003).

2.3. Adsorption experiments

Adsorption experiments with activated and inactivated sludge were performed to distinguish pure adsorption processes and biosorption. Activated sludge from a low loaded municipal wastewater treatment plant with a F/M ratio of 0.01 kg BOD kg TSS⁻¹ d⁻¹ was used. The inactivation of the sludge was implemented with 0.5 ml l⁻¹ mercury(II)sulphate (Hg₂ · SO₄, 200 g l⁻¹). Sludge inactivation was controlled by monitoring the oxygen concentrations, assuming that no oxygen consumption took place, when the inactivation of the sludge was successful. To consider different influences of the experimental setup and preparation, blank samples and internal standards were treated and analysed as the other samples (see Tables 1 and 2).

Table 1

Comparison of theoretical concentrations and mean values and standard deviation ($n = 5$) of measured concentrations

μ_T [mg l ⁻¹]	bisphenol-A			17 β -estradiol			17 α -ethinylestradiol		
	\bar{x} [mg l ⁻¹]	s [mg l ⁻¹]	t	\bar{x} [mg l ⁻¹]	s [mg l ⁻¹]	t	\bar{x} [mg l ⁻¹]	s [mg l ⁻¹]	t
0.10	0.17	0.03	4.839	0.15	0.01	18.779	0.21	0.07	3.833
0.25	0.28	0.02	2.804	0.27	0.04	1.118	0.49	0.08	7.063
0.50	0.52	0.01	3.651	0.49	0.02	0.739	0.90	0.50	1.756
0.75	0.77	0.04	1.087	0.74	0.04	0.542	0.79	0.10	0.862
1.00	0.97	0.09	0.854	0.96	0.08	1.063	0.93	0.08	2.167
2.00	1.97	0.03	2.138	1.95	0.03	3.555	1.97	0.08	0.728
5.00	5.05	0.22	0.503	5.13	0.22	1.334	5.13	0.20	1.525
10.00	10.08	0.79	0.238	10.03	0.68	0.098	9.64	0.35	2.309

Table 2

Initial concentrations, measured values in blank and standard samples (in mg l⁻¹) and calculated recovery rates (in %) for the adsorption experiments

Initial	bisphenol-A			17 β -estradiol			17 α -ethinylestradiol		
	blank	standard	recovery	blank	standard	recovery	blank	standard	recovery
50 ^a	0.98	49.3 ± 2.4	99	n.d.	9.2 ± 0.8	18	n.d.	11.2 ± 1.0	22
25 ^a	0.18	27.1 ± 1.7	108	0.08	10.0 ± 0.5	40	0.08	10.9 ± 0.4	44
10	0.18	9.9 ± 0.2	99	0.08	8.1 ± 1.4	81	0.08	9.6 ± 0.2	99
5	0.13	4.8 ± 0.3	96	0.08	4.5 ± 0.4	90	0.08	4.3 ± 0.6	86
4	0.11	3.5 ± 0.2	88	n.d.	3.4 ± 0.4	85	n.d.	3.5 ± 0.5	88
2.5	0.18	2.4 ± 0.2	96	0.08	2.1 ± 0.2	84	0.08	2.1 ± 0.2	85
2	0.11	1.6 ± 0.1	80	n.d.	1.3 ± 0.1	65	n.d.	1.4 ± 0.2	70
1	n.d.	1.2 ± 0.4	120	0.11	0.71	71	0.13	0.7 ± 0.1	70
0.055000	0.000116	0.054835	100	—	—	—	—	—	—
0.011250	0.000075	0.014300	127	—	—	—	—	—	—
0.001000	n.d.	0.001012	101	n.d.	0.000769	77	—	—	—
0.000500	—	—	—	n.d.	0.000440	88	n.d.	0.000591	118
0.000250	—	—	—	—	—	—	n.d.	0.000329	132
0.000060	—	—	—	n.d.	0.000073	122	—	—	—
0.000025	—	—	—	—	—	—	n.d.	0.000027	108

^a Initial concentrations applied in the desorption experiments.

2.4. Adsorption equilibrium

In a first step the adsorption equilibrium time is determined. After a certain contact time a dynamic equilibrium and a defined distribution of the adsorbate between solid and liquid phase is reached. For the experimental determination of the required contact time Erlenmeyer flasks were filled with 100 ml of inactivated sludge and shaken at 125 rpm. Samples were taken in regular time intervals and the concentration in the liquid phase was determined with the described HPLC method. Prior to analysis the samples were filtered with fluted filters and membrane filters (0.45 μ m).

2.5. Adsorption tests with activated and inactivated sludge

All tests were performed with TSS concentrations of 1, 3, 5 and 7 g TSS l⁻¹. The volatile fraction was

of $\approx 63 \pm 4\%$ of the TSS. The effectively applied TSS concentration was measured at the end of the experiment by applying a standard method (DIN 38409-1).

Activated and inactivated sludge was filled in Erlenmeyer flasks. The sludge quantity was chosen dependent on the adjusted concentration. 100 ml of sludge were used for the high concentration range (initial concentrations higher than 1 mg l⁻¹), whereas total volumes of 800–500 ml were applied for the experiments in the lower concentration range (initial concentrations lower than 1 mg l⁻¹). Different total suspended solids (TSS) concentrations were achieved by mixing the sludge with tap water.

The samples, including blank and standard samples, were shaken at 125 rpm for 24 h, according to the previously determined equilibrium time. Consequently all samples were filtered and analysed. The samples obtained from experiments with high initial concentrations

($\geq 1 \text{ mg l}^{-1}$) were analysed with HPLC and the samples from experiments with lower initial concentrations with LC-MS/MS.

The description of the adsorption characteristics was done by means of determination of characteristic values and by the computation of isotherms. A frequently used characteristic value for the evaluation of the adsorption behaviour is the specific adsorption coefficient K_D (1 kg TSS^{-1}). This distribution coefficient is defined as the ratio of equilibrium concentrations of a dissolved test substance in a two phase system consisting of an adsorbent and an aqueous phase (Eq. (1)).

$$K_D = \frac{C_s^{\text{ads}}(\text{eq})}{C_{\text{aq}}^{\text{ads}}(\text{eq})} \cdot 1000 \quad (1)$$

$C_s^{\text{ads}}(\text{eq})$, content of the substance adsorbed on the sludge at adsorption equilibrium (mg g TSS^{-1}),
 $C_{\text{aq}}^{\text{ads}}(\text{eq})$, mass concentration of the substance in the aqueous phase at adsorption equilibrium (mg l^{-1}).

Other characteristic parameters used to describe the adsorption capacity of a certain adsorbing agent are K_{OM} and K_{OC} values. The K_{OM} (1 kg VSS^{-1}) relates the K_D value to the organic matter of the sorbent (Eq. (2)), whereas the K_{OC} (1 kg OC^{-1}) refers to the organic carbon content (f_{OC}) of the sorbent, as described in Eq. (3). Especially for non-ionic chemicals those specific adsorption coefficients are suitable to describe the adsorption behaviour (Schwarzenbach et al., 1993). Sewage sludge consists of a complex matrix of extracellular polymeric substances (EPS) including a mixture of fats, proteins, amino acids, sugars, carbohydrates, lignin, celluloses, humic material and fatty acids, differing from plant to plant. The described specific adsorption coefficients normalized to the organic matter or the organic carbon content of the adsorbent allow the comparisons of results obtained for different sludges,

$$K_{\text{OM}} = K_D \cdot \frac{\text{TSS}}{\text{VSS}} \quad (2)$$

TSS, total suspended solids concentration (g l^{-1}),
 VSS, volatile suspended solids concentration (g l^{-1}).

$$K_{\text{OC}} = K_D \cdot \frac{100}{\% \text{OC}} \quad (3)$$

%OC, percentage of organic carbon in the sludge sample (g g^{-1}).

Additionally to the mentioned distribution coefficients the adsorption isotherm according to Freundlich was determined (Eqs. (4) and (5)).

$$C_s^{\text{ads}}(\text{eq}) = K_F \cdot C_{\text{aq}}^{\text{ads}}(\text{eq})^{1/n} \quad (4)$$

$$\log C_s^{\text{ads}}(\text{eq}) = \log K_F + 1/n \cdot \log C_{\text{aq}}^{\text{ads}}(\text{eq}) \quad (5)$$

K_F , Freundlich adsorption coefficient [$\text{mg}^{1-1/n} (\text{dm}^3)^{1/n} \text{ g}^{-1}$],
 $1/n$, regression constant.

In the case of a linear isotherm ($1/n = 1$) the Freundlich adsorption coefficient K_F corresponds to the K_D value. The implementation of the experiments and the evaluation of the data was done according to several guidelines (ISO/CD 18749, 2001; OECD/OCDE 106, 2000; OECD/OCDE 121, 2001). The parameter estimation occurred by fitting the experimental determined results to the adsorption model (Freundlich). This was done by regression analysis using the *Signaplot* program (© SPSS Inc.) including a statistical evaluation of the calculated results.

2.6. Influence of pH on adsorption

These experiments were performed in the high concentration range (mg l^{-1}). The experiments aimed to give a qualitative estimation of high pH effects on the adsorption of the investigated compounds and not in a detailed description of desorption kinetics. During wastewater treatment high pH values occur in the sludge dewatering process, if limestone is used for sludge conditioning.

1000 ml inactivated sludge were inoculated with 50 mg of the investigated substance and shaken for 24 h at 125 rpm. The liquid concentration of the substance was measured and the adsorbed fraction was calculated from the difference between those measured values and the applied substance amount, considering the recovery rate of the blank samples without sludge. Thus, the maximum adsorption rate was defined. The sludge activity was controlled via oxygen demand. Subsequently the sludge was divided in 100 ml samples and different pH values were installed using hydrochloric acid (HCl) and/or sodium hydroxide (NaOH). The selected pH values lay in a range from pH 3 to pH 12 ($n = 8$). The reaction time was set once more with 24 h. During this time the Erlenmeyer flasks were shaken at 125 rpm. Then samples were taken, filtered and analysed with HPLC. Additionally the TSS was measured for each sample.

High pH values occur in wastewater treatment plants due to the application of limestone for sludge conditioning. Therefore the experiment was repeated using milk of lime for pH adjustment. The initial experimental concentrations of the investigated substances were adjusted to 25 mg l^{-1} . The objective of this experiment consisted in determining if the lime flocs have an additional adsorption potential resulting in lower desorption rates.

From this experiment also estimates for the pK_a of the investigated compounds were deduced. The pK_a indicates the pH value, for which 50% of a substance is

dissociated and 50% is not dissociated. The data evaluation was done graphically by setting the initial concentration equal to 100% and the achieved equilibrium concentration equal to 0%. The adsorbed fraction was calculated as described before, and the prior mentioned maximum adsorption set equal to 100%.

3. Results and discussion

3.1. Analytical method

To evaluate the accuracy of the HPLC method and to estimate the influence of the experimental setup and the sample preparation (filtration), multiple standard solutions ($n = 5$) of different concentrations were analysed. According to the procedure for the adsorption tests, the samples (spiked tap water) were shaken over a period of 24 h at 125 rpm, filtered with fluted filters and membrane filters (0.45 μm) and analysed. The difference between the experimentally determined mean values ($n = 5$) and the theoretical value μ_T was examined with a t -test (Köhler et al., 1995). The results are summarised in Table 1. The reference t -value for an error probability of 5% and a degree of freedom of 4 amounts to $t_{\text{TAB}} = 2.776$ (Köhler et al., 1995). All calculated t -values higher than t_{TAB} indicate a statistically significant variation from the theoretical value. Especially in the concentration range below 0.5 mg l^{-1} the measured values differ notably from the theoretical value, limiting the applicability of the HPLC method, whereas the results in the lower concentration ranges measured with LC-MS/MS showed good concordance.

For concentrations higher than 0.5 mg l^{-1} the measured values match the theoretical concentrations. As the samples were treated according to the experimental

procedure for the adsorption experiments, no significant influence of the experimental setup or the filtration can be observed.

3.2. Adsorption equilibrium

The contact time necessary to reach equilibrium differed for the different investigated substances. The equilibrium reaction time was of ≈ 2 h for BPA, of 8–10 h for EE₂ and of about 24 h for E₂. To follow a consistent method, all adsorption experiments were performed with a contact time of 24 h.

3.3. Adsorption tests with activated and inactivated sludge

Applied initial concentrations and measured concentrations in blank and standard samples as well as calculated recovery rates are summarised in Table 2. The results summarised in Tables 1 and 2 indicate the negligible influence of the filter material. In the standard samples estrone was found too, although this substance was not added and not detected in the blank sample. The sum of estradiol and estrone on a molecular basis corresponds approximately to the spiked amount, wherefore an oxidation of estradiol to estrone seems to have occurred in the standard sample. To avoid an overestimation of the adsorption potential the measured concentrations of the investigated compounds in the standard samples were used as reference concentrations for the calculations.

As mentioned before the adsorption experiments were performed with activated and inactivated sludge in order to distinguish pure adsorption processes and biosorption. Fig. 1 shows the results of the Freundlich linearization according Eq. (5) for the two adsorbent agents and bisphenol-A. No significant difference

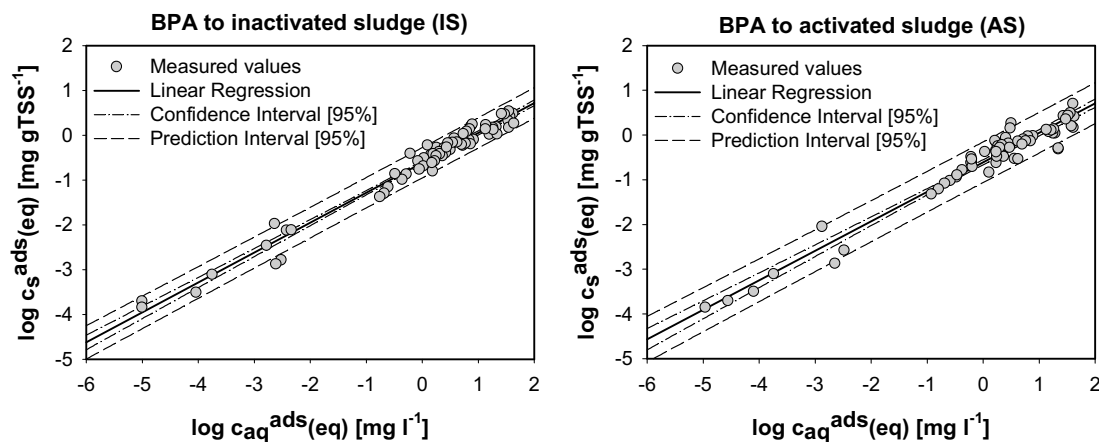


Fig. 1. Adsorption of bisphenol-A to activated and inactivated sludge—linearization according to Freundlich (Eq. (5)).

Table 3

Results of the linearization according to Eq. (5)

Substance	Parameter	Coefficient	Std. err.	<i>t</i>	<i>P</i>	<i>r</i> ²	95% conf. lim.	95% conf. lim.
BP-A	log <i>K</i> _F	−0.6142	0.0198	−30.9927	<0.0001	0.9730	−0.5618	−0.6666
	1/ <i>n</i>	0.6678	0.0132	50.5813	<0.0001		0.6564	0.6792
E ₂	log <i>K</i> _F	−0.2063	0.0532	−3.8802	0.0002	0.9450	−0.0801	−0.3326
	1/ <i>n</i>	0.8999	0.0267	33.6681	<0.0001		0.8816	0.9182
EE ₂	log <i>K</i> _F	−0.3143	0.0503	−6.2419	<0.0001	0.9670	−0.2014	0.4272
	1/ <i>n</i>	0.9337	0.0230	40.5237	<0.0001		0.9186	0.9489

between activated and inactivated sludge is detectable. These observations lead to the conclusion, that within the first 24 h for activated and inactivated sludge adsorption is equal. Within that period adsorption to sludge flocs is an important first step for further degradation of the substance, as obvious in full-scale WWTPs (Kreuzinger et al., 2003).

Similar results were obtained for 17 α -ethinyl-estradiol. For 17 β -estradiol no feasible results were obtained for the activated sludge, as no defined initial conditions can be established, because E₂ metabolizes (e.g. to estrone, which is further degraded) at the time it gets in contact with sewage sludge (Ternes et al., 1999). No saturation level could be reached for the investigated substances during the experiments, in spite of using very high initial concentrations, indicating a high adsorption potential of sewage sludge for those compounds. The calculated parameters characterising the Freundlich isotherm for the different substances and the inactivated sludge are summarised in Table 3.

Additionally the specific adsorption coefficient *K*_D and the distribution coefficients normalized to the organic matter *K*_{OM} and the organic carbon content *K*_{OC} of the adsorbent were calculated (see Table 4).

In the case of bisphenol-A the specific adsorption coefficients are concentration dependent, decreasing with increasing free concentrations. The calculated *K*_D values for the estrogens showed high variation in the concentration range between 0.1 and 0.5 mg l^{−1}, because of the low sensitivity of the applied HPLC method within this concentration range (see Table 1). The standard error of this alternative analytical method increased with lower concentrations. The values reported in Table 1 refer to tap water. The samples obtained from

the adsorption experiments obviously were in contact with the adsorbent agent sludge. The influence of this matrix definitely reduced the sensitivity of the HPLC method leading to strong variations of the results obtained within the mentioned concentration range.

The adsorption coefficients calculated for the hormones are log-normal distributed, wherefore in Table 4 the median value and the limits of the 95% confidence interval are indicated.

The concentration dependency of the adsorption behaviour of bisphenol-A is illustrated by means of the correlation between the specific adsorption coefficients *K*_D, *K*_{OM} and *K*_{OC} and the dissolved equilibrium concentration.

In addition to these batch equilibrium experiments log *P*_{OW} and log *K*_{OC} values were determined according to OECD guidelines (OECD/OCDE 117, 1989; OECD/OCDE 121, 2001). This HPLC method resulted in considerable lower *K*_{OC} values for the investigated compounds than the reported experiments. The log *P*_{OW} (log *K*_{OC}) values were calculated with 2.30 (2.17) for BPA, 2.43 (2.31) for E₂ and 2.69 (2.55) for EE₂ respectively. Compared to literature data, especially the log *K*_{OC} values are low. Staples et al. (1998) indicated log *P*_{OW} values of 2.20–3.82 and a log *K*_{OC} for sediments and soils of 3.20 for BPA. The log *P*_{OW} of 2.20 for BPA was also determined according to the HPLC method and corresponds to the reported value. For ethinyl-estradiol Schweinfurth et al. (1997) indicated a log *P*_{OW} of 4.20, which is significantly higher than the value given above. Lai et al. (2000) published a log *K*_{OC} value of 3.80 for this synthetic estrogen. This value differs notably from the value determined with the HPLC method according to OECD 121, but corresponds to the results illustrated in Table 4. Lai et al. (2000) state the log *K*_{OC}

Table 4

Specific adsorption coefficients *K*_D [l kg TSS^{−1}], *K*_{OM} [l kg VSS^{−1}] and *K*_{OC} [l kg OC^{−1}] for the investigated substances

Substance	log <i>K</i> _D			log <i>K</i> _{OM}			log <i>K</i> _{OC}		
	Median	95% conf.	95% conf.	Median	95% conf.	95% conf.	Median	95% conf.	95% conf.
E ₂	2.84	2.64	2.97	3.02	2.83	3.15	3.30	3.11	3.43
EE ₂	2.84	2.71	3.00	3.03	2.89	3.18	3.31	3.16	3.46
BP-A	log <i>K</i> _D = −0.3403 · log <i>c</i> _{aq} + 2.4110			log <i>K</i> _{OM} = −0.3464 · log <i>c</i> _{aq} + 2.6175			log <i>K</i> _{OC} = −0.3465 · log <i>c</i> _{aq} + 2.8932		

for estradiol with 3.50 and Jürgens et al. (1999) indicate $\log K_{OC}$ values in a range between 2.78 and 3.40. Applying the formula of Sabljic et al. (1995), relating the P_{OW} to the K_{OC} for hydrophobic, non-polar organic substances, values of about $\log 3.50$ were obtained for EE₂. These values for the hormones as well as the ones reported in Staples et al. (1998) for bisphenol-A are higher than the results obtained with the HPLC method according to the OECD guideline but correspond to the experimentally determined adsorption coefficients summarised in Table 4.

3.4. Influence of pH on adsorption

After a contact time of 24 h at pH 7 the residual concentrations in the liquid phase were measured and the correspondent adsorption was defined as maximum achievable adsorption (100%). No desorption was detected below pH 9. A definite desorption occurred for all tested compounds at pH values above 10. 30–50% of the initially adsorbed quantity was released. A second experiment confirmed these results. In course of the experiments, desorption processes occurred at pH levels between 9 and 10 without any time dependency. The pH adjustment within those experiments was achieved with caustic soda.

Comparable high pH values occur in STPs in the sludge treatment process, especially during sludge dewatering. Limestone or milk of lime is often used for sludge conditioning. The precipitating lime flocs represent an additional potential adsorbent for released or desorbed substances, wherefore the experiments were repeated using milk of lime for pH adjustment. The results are represented in Fig. 2 and confirm the results of the precedent experiments.

Desorption starts at pH values higher than 9. Nearly the whole applied Bisphenol-A is recovered in the liquid

phase at pH of ≈ 12 . This leads to the conclusion, that the overall adsorbed quantity is released at these high pH values. No differences in the desorption behaviour can be detected after different reaction times (4.5; 24 h, see Fig. 2). Influence of pH on the solubility of the substances was assessed by recovery rates in blind samples without sludge. Whereas for bisphenol-A equal solvability was measured at different pH values, an increasing solubility was detected for E₂ and EE₂ between pH 7 and pH 12. At pH 7 the measured concentrations of the steroid hormones correlated with the solubility values reported in Tabak et al. (1981). At pH 11.9 the recovery rate in the blank sample of E₂ was evaluated with 103% (initial concentration 25 mg l⁻¹) and 84% (initial concentration 50 mg l⁻¹) and 84% (initial concentration 50 mg l⁻¹) indicating higher solvability at higher pH. For EE₂ a similar recovery rate of 111% was detected at an initial concentration range of 25 mg l⁻¹, whereas the recovery at an initial concentration of 50 mg l⁻¹ amounted to 52%. By means of the experiment's duration of 24 h a release of the precipitated fraction occurs due to adsorption of the initial solved concentration and subsequent resolution of the formerly precipitated fraction.

About 80% of the initially adsorbed mass is released at high pH values. Such releases of adsorbed compounds after sludge dewatering result in a high backloading of the STP via the supernatant recycle.

From these experiments estimates for the pK_a value can be derived. The results of the evaluation are shown in Fig. 3 (BPA and EE₂).

The deduced pK_a values correspond well to literature data. From bisphenol-A a pK_a of 10.3 is calculated. Staples et al. (1998) indicate pK_a values for BPA of 9.6, 10.2 and 11.3 in their review, according to different literature sources. A pK_a value of about 10.4 was determined for 17 β -estradiol and of about 10.7 for 17 α -ethinylestradiol. These values are within the range

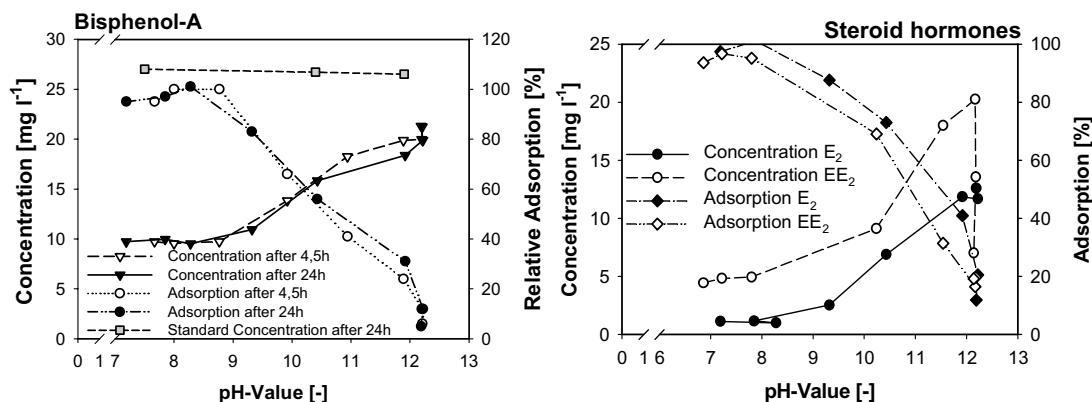


Fig. 2. Concentrations (mg l⁻¹) of the investigated substances and relative adsorbed amount (%) to inactivated sludge in dependency on the pH using milk of lime for pH adjustment.

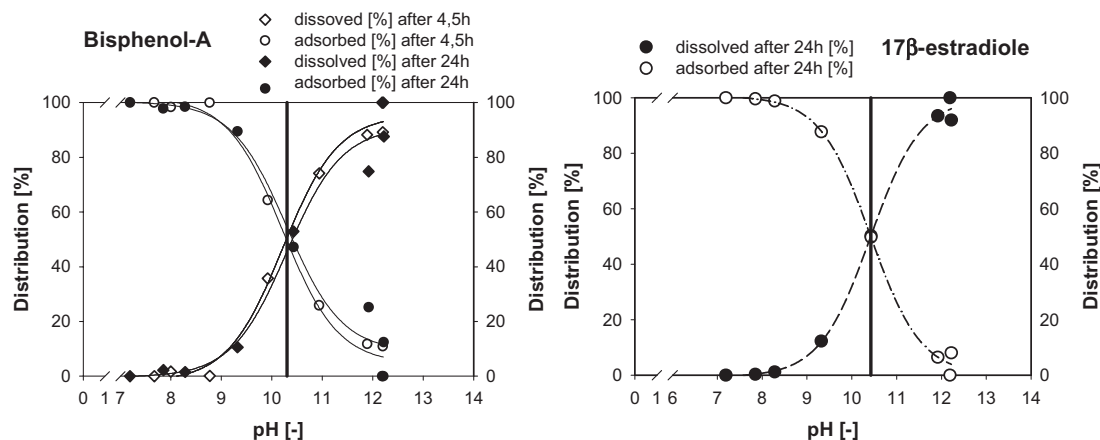


Fig. 3. Distribution of bisphenol-A and 17 α -ethinylestradiol between liquid and solid phase in dependency on the pH.

stated by Hurwitz and Liu (1977). There the pK_a values were determined experimentally and indicated with 10.46 ± 0.03 for E_2 and with 10.40 ± 0.01 for EE_2 .

4. Conclusions

The illustrated results represent basic information on the sorption behaviour of bisphenol-A, 17 α -ethinylestradiol and 17 β -estradiol to sewage sludge. As the adsorption to the sludge and the removal via excess sludge abstraction is one important elimination pathway, such information is essential for a quantitative description. A high adsorption potential to sewage sludge could be observed for all investigated substances. Saturation was not reached in any of the experiments, even applying high initial concentrations. Substances with $\log K_D$ values lower than 2 are negligible for adsorption. For substances with $\log K_D$ values higher than 4, sorption to the sludge is a major removal process. All investigated substances show K_D values between these boundaries and proof to be relevant for this removal pathway. During sludge treatment high pH values can occur if lime is used within this process (e.g. for sludge conditioning). At high pH values a release of the adsorbed fraction to the liquid phase was observed for the investigated compounds. Desorption occurred at pH values in the range of the pK_a values of the observed chemicals. Beside pure adsorption processes also biological transformations and degradation occurs. As degradation is dependent on the operated sludge retention time, especially in highly loaded systems (F/M ratio > 0.5), the removal of substances with high adsorption potential predominantly is determined by the abstracted mass via excess sludge. In such plants a relevant backloading via the recycle of the supernatants can be expected. Such different conditions have to be

considered in the assessment of achievable removal efficiencies of STPs regarding the discussed substances.

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